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14. ABSTRACT
A novel multiscale simulation methodology was developed for the fields of nanotechnology and soft materials. The overall aim was to develop a systematic inverse coarse-graining (ICG) approach designed to bridge theoretical [3]intuitive[2] models of the previously mentioned systems with real, atomistic-level descriptions. The objective of this research was to develop a robust ICG capability within a framework well-founded in statistical mechanics, molecular dynamics, and multiscale coarse-graining simulation. The multiscale coarse graining (MS-CG) method formed a key framework for the ICG strategy. Detailed atomistic-level simulations provided the initial template by which to construct a diverse set of coarse-grained [3]building blocks[2]. This research project represented a significant step forward for Air Force priorities in the areas of nanotechnology and energetic materials such as ionic liquids. The ability to computationally predict detailed atomistic-level models from highly abstracted minimalist models opened up the possibility for real systems to be developed in a [3]tunable[2] fashion, without exhaustive experimental synthesis and design searches. The ICG methodology provides a critical link between molecular modeling and real materials design.

15. SUBJECT TERMS
Theoretical Chemistry, Ionic Liquids, Molecular Modeling, Coarse-graining, Materials Design

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Final Performance Report

In this AFOSR project a very important set of atomistic and coarse-grained (CG) molecular dynamics (MD) simulations were designed and performed to study the structure and dynamical properties of room temperature ionic liquids (ILs). Eight papers in total were published during the grant period.[1-8] Overall, a number of particularly high impact and ground-breaking publications have come out of this body of research, including a review[3] in a Special Issue of Accounts of Chemical Research devoted to ionic liquids that the PI was invited to co-edit. As an example of this work, the behavior of the ionic liquid/vacuum interface was studied by applying the MS-CG method.[4] When the alkyl chain length of the IL cation was increased, a simple monolayer ordering was shown to change over to a unique multilayer ordering at the IL interface, while the surface tension decreased and approached a constant value, consistent with Langmuir theory and experiment.

A detailed orientational study demonstrated that the alkyl chain of the IL cations prefers to align parallel to the surface normal while the aromatic ring tends to be perpendicular to the surface normal. The surface electron density profile showed that the surface electron density oscillations are mainly contributed by the cations. Figure 1 (a) through (d) (shown at right) depicts the results for the 1-dodecyl-3-methylimidazolium/NO_3^- system, revealing a clear multilayer ordering. Shown are: (a) all CG sites; (b) CG sites of aromatic rings, the CH_3 groups on long side chains and anions; (c) CG sites of the CH_3 groups on long side chains; and (d) CG sites of aromatic rings and anions. MS-CG models of bulk 1-alkyl-3-mehtylimidazolium-based (ILs) with alkyl substituents of different lengths were also developed and applied to predict novel nanoscale spatial heterogeneity.[2] Similar results obtained for water-IL liquid mixtures exhibited unique nanostructural micelle formation phenomena.[1] These results also applied to the model energetic ionic liquid HEATN,

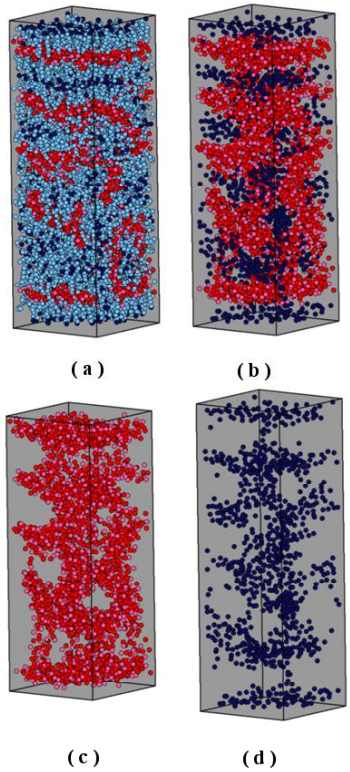

Figure 1. Spatial heterogeneity and charge layering of an IL interface (top layers). See text for details.

where a pronounced glassy behavior was revealed that related to this IL's different chemical structure.[5]

An effective force coarse-graining (EF-CG) method was also developed to construct transferable coarse-grained IL force fields.[7] In the EF-CG method, the effective pairwise forces between CG sites are calculated by taking the average of the atomistic forces between the corresponding atomic groups in configurations sampled from equilibrated atomistic MD simulations. When compared with the more general multiscale coarse-graining (MS-CG) method, the EF-CG method retains the transferable part of the CG potential with the cost of a slightly reduced structural accuracy, but with the gain of a substantially simpler algorithm. In contrast to the MS-CG approach, the EF-CG method therefore determines CG force fields with higher transferability, but with reduced structural accuracy.

As an example, in Fig. 2 the EF-CG 1-ethyl-3-methylimidazolium ($EMIM^+$)/NO_3^- system is shown for (a) the all-atom and (b) EF-CG models for EMIM/NO_3^-. Figure 3 below shows the comparison of radial distribution functions (RDFs) for different CG sites between the EF-CG and all-atom MD results.

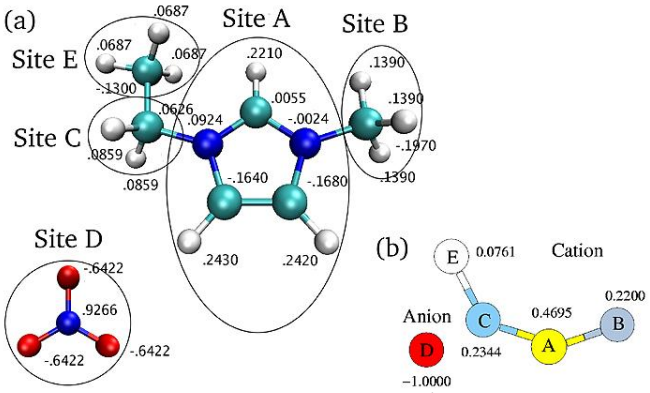

Figure 2. CG model for the ($EMIM^+$)/NO_3^- ionic liquid.

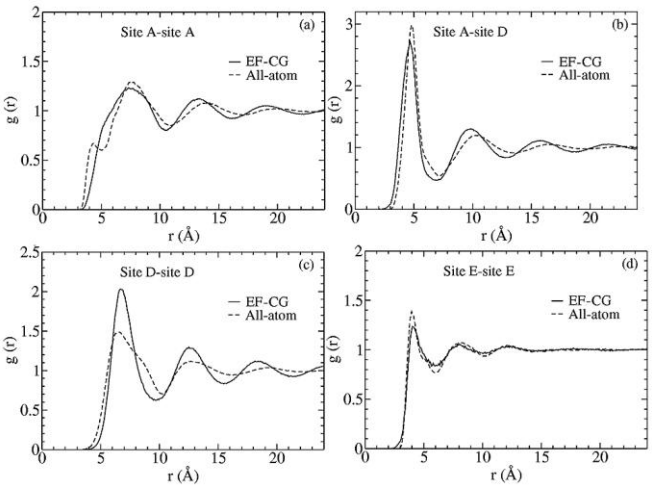

Figure 3. Comparison of RDFs for the EF-CG and all-atom MD simulations for the ($EMIM^+$)/NO_3^- ionic liquid.

The transferability of the EF-CG force field was then studied for different ionic liquid structures and different temperatures.[7] A single EF-CG IL model was successfully used to reproduce the structures and properties of other ILs possessing different side chain lengths. The EF-CG simulations, at different

temperatures, further revealed that the EF-CG force fields have very good transferability over the temperature range studied (298K-700K).[7] An "inverse coarse-graining" methodology was further developed to determine the underlying atomistic structures from the CG model simulations.[6]

All in all, this AFOSR-supported research project on inverse CG modeling as applied to ionic liquids proved to be a very successful effort that was in many ways also groundbreaking for both the IL and molecular modeling fields. It was also an opportunity to broaden the funded research into a new and challenging direction, congruent with evolving Air Force priorities.

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